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SYNTHESIS OF TETRAPHENYL STANNACYCLOPENTADIENES (STANNOLES) III--ETC(U)
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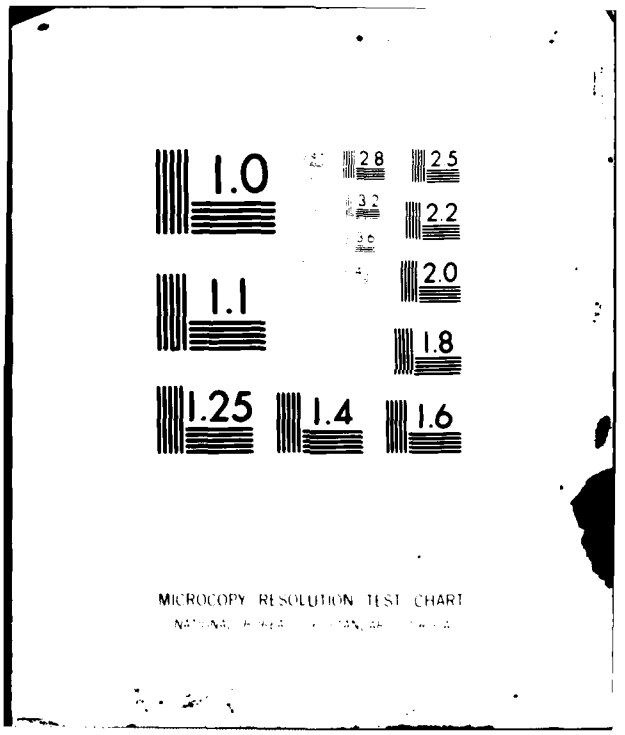
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SYNTHESIS OF TETRAPHENYLSTANNACYCLOPENTADIENES (STANNOLES). III. ATTEMPTED ROUTE TO THE PARENT STANNOLES THROUGH CLOSURE OF 1,4-DICHLOROBUTA-1,3-DIENE[1]

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ABSTRACT

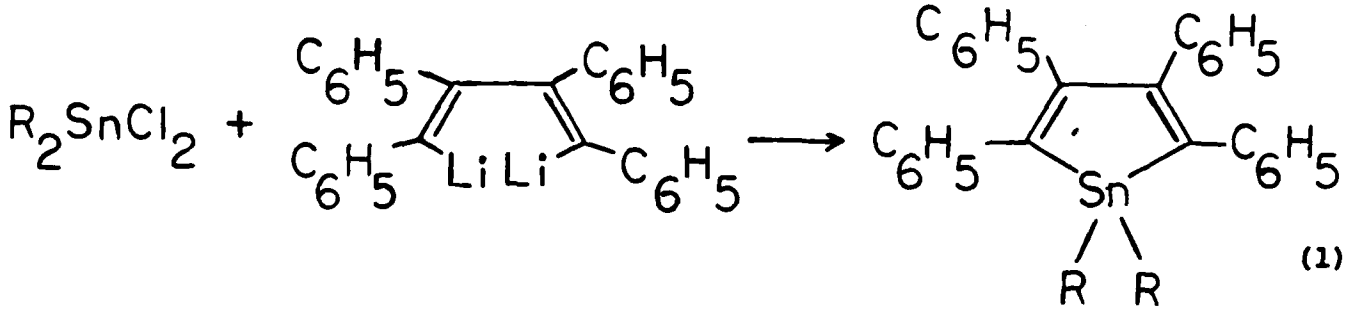
1,4-Dichlorobuta-1,3-diene has been lithiated and reacted with organosilyl and tin chlorides. Only polymerized starting material, rather than the hoped for parent sila- and stannacyclopentadienyl (silole and stannole) ring systems result from the action of the lithiated material on diorganodichlorosilanes and diorganotin dichlorides. Addition of the lithiated butadiene to trimethylchlorosilane and trimethyltin chloride yields products resulting from dehydrochlorination and multiple bond migration in the starting dichlorobutadiene.

INTRODUCTION

Variously 1,1-disubstituted stannoles based upon the 2,3,4,5-tetraphenylstannacyclopentadiene system have been synthesized and reported as part of this series of papers.[1-2] The parent stannole ring system is, however, unknown.

One possible approach is through the 1,4-dilithio derivative of the unsubstituted butadiene-1,3 by analogy with the now well-

known and general reaction of the cis-,cis-1,4-dilithio-1,2,3,4-tetraphenylbutadiene with organometallic and metalloidal dihalides. The reaction of diorganotin dihalides, for example, affords a convenient route to the stannoles:[3-6]



(1)

+ 2 LiCl

The dihalo- precursor to the simple dilithio compound, 1,4-dichlorobuta-1,3-diene, can be prepared by the dimerization of 1,2-dichloroethylene with benzoyl peroxide and dechlorination of the resulting 1,3,4,4-tetrachlorobut-1-ene by metallic zinc dust in methanol:[7-10]

$$2\ ClHC{=}CHCl \xrightarrow[\text{peroxide}]{\text{benzoyl}} ClHC{=}CHCHClCHCl_2 \xrightarrow[2\ CH_3OH]{Zn} ClHC{=}CHCH{=}CHCl \quad (2)$$

The infrared spectrum of the product shows the superimposition of bands arising from the cis-,cis-; cis-,trans- and trans-,trans- isomers of 1,4-dichlorobuta-1,3-diene.[7] The mass spectrum contains the parent ion as a polyisotopic peak at m/e = 126.

RESULTS AND DISCUSSION

Unfortunately, treatment of the 1,4-dichlorobutadiene with methyllithium followed by addition of either diorganodichlorosilanes or diorganotin dichlorides results only in the polymerization of the starting material. The infusible white solid polymer leaves no silicon or tin(IV) oxide residue on burning, and exhibits in its infrared spectrum absorption bands at 1638 cm^{-1} arising from a-C=C- stretching mode, a second band at 842 cm^{-1} which can be assigned to a δ(C-H) out-of-plane deformation mode and a broad band centered at 650 cm^{-1} from a ν(C-Cl) mode. Carbonylation of the expected 1,4-dilithio intermediate with carbon dioxide did not give an unambiguous 1,4-dicarboxylic acid product on hydrolysis, but instead an intractible mixture. Neither did reaction of trimethylchlorosilane or trimethyltin chloride give the expected 1,4-bis (trimethylmetalloidal) derivatives.

Addition of the 1,4-dichlorobutadiene lithiated by methyllithium to a solution of trimethylchlorosilane in ether gave a precipitate and a filtrate from which two silicon-containing products could be isolated, 1,4-bis(trimethylsilyl)buta-1,3-diyne, and what appears to be a trace of a product deriving from 1-trimethylsilylbuta-1-yne-3-ene which could not be identified:

$$ClHC{=}CHCH{=}CHCl + 2CH_3Li \xrightarrow[-LiCl]{(CH_3)_3SiCl} (CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3 \qquad (3)$$

This reaction is similar to that when 1,2-dichloroethylene is treated with methyllithium followed by trimethylchlorosilane to give 1-trimethylsilyl-2-chloroacetylene:[11]

$$ClHC{=}CHCl + CH_3Li \xrightarrow{-CH_4} LiHC{=}CHCl \xrightarrow[-LiCl,-HCl]{(CH_3)_3SiCl} (CH_3)_3SiC{\equiv}CCl \qquad (4)$$

1,4-Bis(trimethylsilyl)buta-1,3-diyne has been synthesized by the dimerization of ethynyltrimethylsilane by the copper(I) chloride tetramethylethylenediamine complex in the presence of oxygen gas.[12,13]

Analogous reaction of the lithiated 1,4-dichlorobutadiene with trimethyltin chloride gave only one tin-containing product, 1,4-bis-(trimethyltin)butatriene, along with a large yield of the polymerized 1,4-dichlorobutadiene:

$$ClHC{=}CHCH{=}CHCl + 2CH_3Li \xrightarrow[-2CH_3Cl]{} \xrightarrow[-LiCl,\ -HCl]{(CH_3)_3SnCl} (CH_3)_3SnCH{=}C{=}C{=}CHSn(CH_3)_3 \qquad (5)$$

Thus both the silicon and tin reactions result in products which derive from dehydrochlorination and multiple bond migration in the starting 1,4-dichlorobutadiene.

EXPERIMENTAL

1,1,2,4-Tetrachlorobut-1-ene

1,2-Dichloroethylene (430 g cis- and trans-mixture, 4.44 moles, b.p. 56-62°) was allowed to reflux for 14 days with dibenzoyl peroxide (4.5 g, 18.6 mmoles). After the removal of unreacted starting material, distillation gave the following fractions:

b.p. 40-84.2° (18.5 mm), 10 g; b.p. 84.2-94.0° (18.5 mm), 160 g and b.p. 94.0-94.3° (18.5 mm), 1 g (lit. b.p. 80-83°/14 min;[9] 80-82°/15 mm,[10] 195/atm[10]).

Dechlorination

A solution of 1,1,2,4-tetrachloro-butene (140 g, second fraction, 0.73 mol) in methanol (140 mL) was added dropwise in the course of 105 min to a stirred suspension of zinc dust (315 g, 4.82 g-atoms) in methanol (420 mL). Toward the end of the addition the mixture was allowed to reflux gently. After stirring 24 hr at room temperature the hydrochloric acid solution was extracted with methylene chloride. Drying and evaporation of the organic solvent gave an oil which on distillation gave the following fractions: b.p. 29.5-37.0° (15-25 mm), 8.0 g; b.p. 31.5-35.0° (16.5 mm), 60.0 g and b.p. 35.0-60.0° (16.5 mm), 5.2 g (lit. 28°/15 mm[9]). The total yield was 73.2 g (82% of theory) of the combined fractions, previously shown to consist of different isomeric forms of the product,[7,9] which was used for all subsequent work.

The infrared spectrum showed bands at 3085(s), 3065(s), 1755(m,b), 1702(m,b), 1671(m,b), 1623(s), 1568(s), 1355(m), 1336(s), 1304(s,d), 1240(w), 1184(m,d), 1115(m), 1092(m), 950(s,sh), 910(m), 845(s), 805(s,sh), 765(s,b), 710(s), 598(m) and 495(m) cm^{-1}. The mass spectrum contained fragments up to m/e = 126 which is the molecular ion. An abundant dichlorine-containing peak appeared at m/e = 122.

Reaction of Lithiated 1,4-Dichlorobuta-1,3-diene with Trimethylchlorosilane

Methyllithium in ethyl ether (8.00 mL, 13.36 mmoles) was added dropwise to an ether solution of 1,4-dichloro-1,3-butadiene (2 g, 16.3 mmoles). The reaction was cooled in a Dry Ice/acetone bath under nitrogen and the temperature slowly raised to ambient. The brown-colored solution gave a light-brown colored suspension after stirring at room temperature for 2 hrs. The lithium solution was added dropwise at -70° to a solution of trimethylchlorosilane (4.1 mL, 32.0 mmoles) in ethyl ether (5 mL), and the temperature slowly raised to ambient. Refluxing 30 minutes gave a tan colored precipitate for which the infrared spectrum lacked the stretching frequency associated with the Si-$(CH_3)_3$ group at 750 cm^{-1}.

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5-42.5°(16.5 mm), 1.1 g (1,4-dichlorobuta-1,3-diene); b.p. 75-78.0° (15 mm), 0.3 g and b.p. 90-92.5°(10 mm), 0.9 g [1,4-bis(trimethylsilyl)buta-1,3-diyne] in 28% yield.

The third fraction collected at 90-92.5° (10 mm) was found to be 1,4-bis(trimethylsilyl)buta-1,3-diyne (mp - 107°; lit.[12-13] = 107°). The infrared spectrum showed bands at 2960(s), 2900(m), 2065(s,sh), 1413(m), 1250(s), 850(s,b), 765(s), 708(m), 650(s), 557(s), 470(w) and 382(s) cm^{-1}. The nmr spectrum for $CDCl_3$ contained only a singlet (lit.[12] = 0.15 ppm) for the trimethylsilyl protons.

The second fraction was separated and collected by gas chromatography [6 ft. column, 10% UC-W98 (silicone oil) 80-100 packing on Chromosorb W]. Its nmr spectrum in $CDCl_3$ contained two singlets at τ 0.18 and 0.14 in addition to the vinyl group proton multiplet. The proton integration ratio was found to be 1:4.4 = vinyl:silylmethyl. The mass spectrum contained fragments up to m/e = 194, with an abundant fragment at m/e = 117. Anal. Found: C, 53.27; H, 7.12%. We are unable to assign a reasonable structure on the basis of this evidence.

Reaction of Lithiated 1,4-Dichlorobuta-1,3-diene with Trimethyltin Chloride

Into a solution of trimethyltin chloride (6.26 g, 32.0 mmoles) in ethyl ether (5 mL) the lithium reagent (13.36 mmoles) prepared as above was added dropwise at -70° and the temperature slowly raised to ambient. Refluxing for 30 minutes gave a light-brown colored precipitate, for which the infrared spectrum lacked the stretching frequency of the $Sn(CH_3)_3$ group at 556 cm^{-1}.

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5-42.5°(16.5 mm), 1.2 g (1,4-dichloro-1,3-butadiene) and b.p. 55.0-58.8°(18.0 mm), 1.5 g (24.8% yield) $[(CH_3)_3SnCH=C=C=CHSn(CH_3)_3]$.

The infrared spectrum of the latter contained bands at 3060(w,sh), 2998(m), 2920(m), 2375(w), 1759(w), 1715(w), 1623(w), 1569(m), 1400(w,b), 1335(w), 1300(w,d), 1194(m), 1120(w), 1092(w), 950(m,sh), 840(m), 790(s,b), 550(s), 515(w) and 325(s,b) cm^{-1}. The

nmr spectrum in $CDCl_3$ contained a singlet at 0.69 ppm with $|^2J(^{119}Sn\text{-}C\text{-}^1H)|$ = 56.1 Hz, with the proton integration ratio of 1:1 = vinyl:methyl vs. 1:9 calcd.

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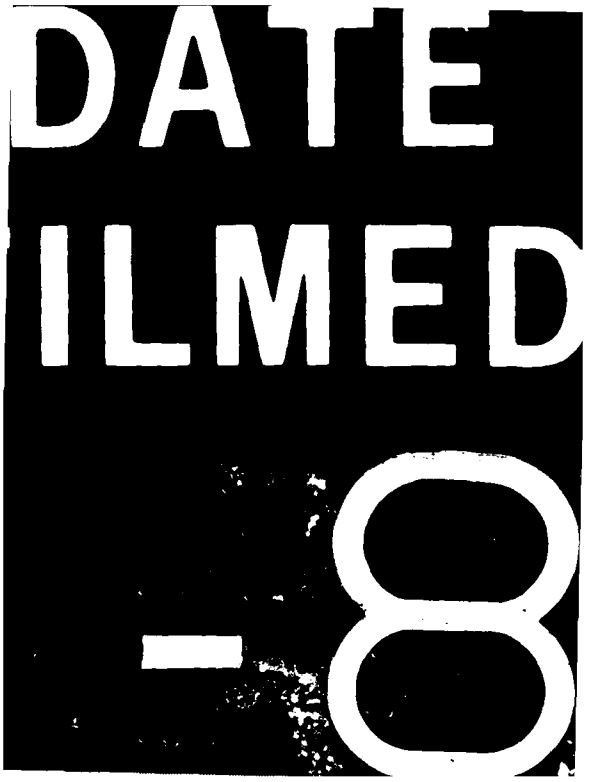
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